SOME FACTORS RELATING TO THE SPECIFICATION OF THE STATE OF GLASS: CRYSTALLIZATION PHENOMENA

BY

ESTHER MILLER TUTTLE

B.S., Alfred University, 1942
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AN ABSTRACT OF A THESIS

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SOME FACTORS RELATING TO THE SPECIFICATION OF THE STATE OF GLASS: CRYSTALLIZATION PHENOMENA

The need for a more adequate specification of the state of glass has been emphasized by the reported disagreement in many cases of physical measurements carried out on the same glass. Such a specification should include information concerning (1) the nature and distribution of the molecular groupings which constitute the random three-dimensional network characteristic of the glassy condition, and (2) the processes which are continually taking place as the glass approaches equilibrium. At the present time such information is primarily qualitative in nature. In a general sense, the moecular groupings in glass are considered dynamic, and diffuse linkages among atoms may result in representatives of every possible arrangement. It is believed that there will be a preponderance of those atomic associations which most completely satisfy the potential requirements demanded of the combination resulting from the interlocking of the various fields of force.

The glassy state is dependent on the ability of a material to be undercooled; so that a regular and repetitive arrangement of atoms to form a crystalline structure does not result. It is believed that the condition of glass may be undercooled not only in relation to crystallization, but also in relation to other processes such as polymerization, formation of colloids, reactions between constituents, diffusion, etc. Crystallization has been considered one of the processes subject to interference in its normal advancement toward equilibrium by the under- or overadvancement of one or more of the processes mentioned above.

A preliminary study of the problem suggested that the manner in which a glass crystallizes should give important information pertaining to the state of glass; it would seem

reasonable that the mechanism of crystallization will vary according to the statistical distribution of the various "molecular species, aggregations or groups" as the glass is subjected to thermal treatment. It is suggested that a study of the linear rate of crystal growth and the incidence of nuclei in the first stages of crystallization may aid in determining the degree to which the reproducibility of the state of a glass may be affected by the previous thermal history and by the presence of small amounts of extraneous elements.

It was the purpose of this work to provide a more critical assessment of some of the factors in relation to the mechanism of crystallization, with the thought in mind that such an assessment may provide a better basis for the specification of the state of glass. To this end an attempt was made to determine the relative effectiveness of thermal treatment and small compositional variations in altering the rate of crystal growth of a glass whose primary phase lies in the wollastonite field of the soda-lime-silica equilibrium diagram.

To determine the linear rate of crystal growth a method was developed to reduce as much as possible the effect of contact of the glass with dust and container surfaces and to eliminate the effect of adjacent crystals forming at widely different temperatures in the same specimen. Glass films, formed on platinum wires, were subjected to a series of thermal treatments below the liquidus temperature of the glass to form and grow crystals. The specimens were then subjected to appropriate petrographic examination. The change in length of the semi-major axis of the crystals formed per unit time represented the linear rate of crystal growth at any one temperature.

The linear rate of crystal growth of a base glass of the theoretical composition, SiO_2-70, Na_2O-15 and CaO-15, was determined by this method. Chemical and spectrographic analyses and index of refraction and devitrification tests were used to indicate as accurately as possible the composition and homogeneity of the base glass. The effect of the addition of

0.5, 1.0 and 2.0 mol percent of zirconium oxide and manganese dioxide on the rate of crystal growth of the base glass was determined at several temperatures betwen 800° C. and 1050° C. By means of a heavy liquid separation of the crushed, devitrified melts and the subsequent spectrographic analysis of the fractions, the degree to which zirconium oxide and cobalt oxide may be taken into the crystal during devitrification was determined. The time required to develop crystals as the temperature was either rising or falling was investigated by means of the film technique.

The use of rate of crystal growth measurements to indicate the reproducibiity of the degree of homogeneity, upon which depends the reproducibility of the state of glass to a large extent was investigated. That the probability of uniformity of both distribution of crystals and rate of crystal growth in glass is associated with a high degree of homogeneity, was indicated by (1) the increase in variation of the refractive index of the glass remaining after devitrification, and (2) the sporadic occurrence of new nuclei after each successive period of heating of an originally homogeneous glass at a temperature below the liquidus point. The following conclusions were drawn from this investigation:

1. Linear rate of crystal growth measurements may give helpful information pertaining to the state of a glass by indicating the reproducibility of its degree of homogeneity.

2. Linear rate of crystal growth measurements are influenced by a probability factor. The degree of homogeneity of the glass remaining after devitrification was considerably lower than that of the original melt and this may contribute to the probability factor in the rate of crystal growth measurements.

3. An improved method for determining the rate of crystal growth in glass was developed to allow greater control of the experimental factors which alter crystallization in glass. The application of the procedure to a wide range of temperature conditions was of particular advantage.

4. It has been shown that small amounts of added oxides may have considerable effect on the linear rate of crystal growth in glass. The addition of zirconium oxide decreased the rate of crystal growth, while manganese dioxide and cobalt oxide promoted the crystallization of wollastonite in the base glass.

5. By means of spectrographic analyses, it was shown that zirconium may be taken up by wollastonite crystals growing in the base glass, while cobalt did not appear to take any appreciable part in the structure of the crystal as devitrification proceeded.

6. For the amount of zirconium oxide present, 0.5 mol percent was more effective in inhibiting the maximum rate of crystallization than the higher percentages, while the effect of manganese dioxide in increasing the maximum rate of growth was almost proportional to the amount of oxide added.

7. The direction from which the crystallization temperature was approached altered the degree of devitrification per unit time of the base glass. At the temperature of maximum crystallization almost 75 times more time was required to develop crystals on cooling down from a temperature above that of liquidus than on a heating up schedule. This was attributed to the probability of the nucleus number, the elimination of nuclei by heating above the liquidus temperature, and the fact that the temperature of maximum nucleation is considerably lower than the temperature of maximum crystallization of the base glass.

VITA

Esther Miller Tuttle was born on April 3, 1920 in Rochester, New York and received her elementary and high school education under the public school system of that city. In 1938 she entered the New York State College of Ceramics at Alfred, New York as an undergraduate and received the degree of Bachelor of Science in Ceramic Engineering in June 1942. In June 1943 she completed the requirements for the degree of Master of Science in Ceramic Engineering under the Edward Orton Jr. Ceramic Foundation Fellowship at the same university. From June 1943 to May 1944 she was employed as assistant spectroscopist by the Oregon State Department of Geology and Mineral Industries, Portland, Oregon and from May 1944 to August 1946 she held the position of spectroscopist with the same department. She matriculated at the University of Illinois in September 1946 under a fellowship granted in the Graduate College of that university.

She is a member of the American Ceramic Society, Keramos, Sigma Xi and Sigma Delta Epsilon.

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